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Implications of Treating Water Containing Polynuclear Aromatic Hydrocarbons with Chlorine: A Gas Chromatographic-Mass Spectrometric Study

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The products of aqueous chlorination reactions of 1-methylnaphthalene, fluorene, dibenzofuran, anthracene, phenanthrene, 1-methylphenanthrene, fluoranthene, and pyrene have been determined. The conditions employed for these reactions approximated those that might be encountered in water treatment facilities. Reactions at pH > 6 tended to produce oxygenated products (epoxides, phenols, quinones, etc.), and reactions at pH < 6 tended to produce both oxygenated (quinones) and chlorinated products.

The use of chlorination as the predominant technique for water renovation and disinfection has been questioned because of the reaction of active chlorine species with organic compounds present in the water to form products which may be biologically harmful (*1-3*). These reactions may occur at the site of chlorine addition as well as throughout a water distribution system (*4*). Polynuclear aromatic hydrocarbons (PAH) have been suggested as the precursors to at least a portion of the mutagens produced in some chlorination processes (*4*). The levels of these ubiquitous PAH compounds may be increased by the presence of coal tar coatings inside pipes and water storage tanks (*5*).

In order to provide further insight into the possible role of PAH in chlorine-induced mutagen formation, this laboratory has continued the study of the aqueous chlorination chemistry of PAH (*6*, *7*). The present report describes a detailed study of the product distributions of several PAH compounds which were chosen for study based on their previous identification in drinking water (*8*). A related study in these laboratories of the reaction kinetics and mechanisms for the aqueous chlorination of phenanthrene, fluorene, and fluoranthene will be reported elsewhere.

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Experimental

Procedure

Twelve liters of water were treated with chlorine gas, and an appropriate amount of sodium hydroxide was added to achieve the desired pH. A solution of the PAH in acetonitrile (40-800 ml, specific conditions in Tables) was added to initiate the reaction which was monitored by HPLC. For high pH solutions, the pH was maintained by periodic addition of NaOH. To this, 2.5-3 equivalents (based on the total chlorine concentration) of dimethyl sulfoxide or sodium thiosulfate were added to terminate the reaction. In some cases, the reactant solution was acidified with sulfuric acid in order to suppress ionization of acidic products. The solution was then forced through two 7 × 50 mm stainless steel adsorption columns connected in series. The first column contained C-18 Porasil B (37-75 μm, Waters Associates), and the second contained XAD-2 (100 μm, Rohm and Haas). Reaction products which were adsorbed were later removed by elution of the column train with acetonitrile and then with methylene chloride. Some separation of these products was observed during the elution process. The various fractions collected were then checked for product content by HPLC and concentrated under a nitrogen stream prior to analysis by gas chromatography-mass spectrometry (GC/MS). Portions of fractions suspected of containing acidic compounds were methylated with diazomethane.

Standards

The following compounds were purchased, checked for purity, and, where necessary, purified by recrystallization, sublimation, and/or preparative reversed phase liquid chromatography: phenanthrenequinone, 9-chlorophenanthrene, 9-fluorenone, 1-chloropyrene.

The following compounds were prepared according to literature methods: *trans*-9,10-dihydro-9,10-dihydroxyphenanthrene (*9*), 2-chlorodibenzofuran (*10*), 2,8-dichlorodibenzofuran, (*10*), phenanthrene-9,10-oxide, (*11*), 2,3-fluoranthenedione (*12*), 3-fluoranthenol (*13*), 2-chlorofluorene (*14*), 3-chlorofluoranthene (*14*), 4-pyrenol (*15*), 9-fluorenone-1-carboxylic acid (*16*), 4,5-pyrenedione (*17*), *cis*-4,5-dihydro-4,5-dihydroxypyrene (*18*), dichloropyrene (*19*, *20*), 1,6-/1,8-pyrenedione (*21*), and 4,5-phenanthrenedicarboxylic acid anhydride (*22*).

9-Phenanthrenol was prepared by the rearrangement of phenanthrene-9,10-oxide with base. Diisopropylamine (0.476g, 0.0047 mmole) and *n*-butyllithium (3.23 ml of 1.6*M* solution in hexane, 0.0052 mole) were combined in tetrahydrofuran (THF) at −78°C under N_2. A slurry of phenathrene-9,10-oxide (0.911 g in THF, 0.0047 mole) was added by syringe and the mixture was then allowed to warm slowly overnight. Sulfuric acid (1*N*) was added, and the mixture was twice extracted with benzene and the combined extracts were dried with magnesium sulfate and evaporated in a rotary evaporator at 30°C. Tan crystals (0.844 g, 92%) resulted with mp 144−147°C. Recrystallization from benzene gave tan crystals, mp 149-151°C (lit. mp 151−152°C) (*23*). IR(KBr) showed the absence of phenanthrenequinone. This phenol undergoes rapid autoxidation to phenanthrenequinone (*24*), at such a rate as to preclude the preparation of pure solutions. The generation of an HPLC standard curve required correction for the amount of quinone present.

9,10-Dichlorophenanthrene was prepared by the chlorination of phenanthrene. Methylene chloride (100 ml) and commercial bleach (100 ml) were combined in a closed container and the pH of the aqueous layer adjusted to 4 with phosphoric acid (*11*). The total chlorine content of the two layers was determined by iodometric titration to be 0.03*M*. Phenanthrene (0.85 g, 0.0048 mole) was added and the mixture stirred at room temperature for 5 hr. The organic layer was then removed, washed with water and saturated with sodium thiosulfate solution, dried over magnesium sulfate and evaporated to yield a yellow solid (80%). Recrystallization from methanol and again from acetonitrile gave tan crystals of mp 157.5-159°C (lit. mp 158-160°C) (*19*); NMR ($CDCl_3$) δ 7.6-8.1 (*m*, 4H), 8.4-9.0 (*m*, 4H).

2,7-Dichlorofluorene was prepared from the bisdiazonium salt. 2,7-Diaminofluorene (1.0 g, 1 mmole, Aldrich Chemical Co.) was placed into 4 ml of water and added to 11 ml of 4.4*N* hydrochloric acid. Sodium nitrate (0.155 g, 2.2 mmole) in 4 ml of water was then added and the resulting mixture was stirred for 1.5 hr at 20°C. This mixture was then added to a slurry of cuprous chloride (0.385 g, 4.3 mmole) in 8 ml of water. After 4 hr at 50°C the resulting solid was removed, taken up into methylene chloride and washed with 1*N* hydrochloric acid, 1*N* sodium hydroxide, and water. The organic layer was then dried over magnesium sulfate and evaporated. Recrystallization of the solid from hexane and then from methanol gave 2,7-dichlorofluorene, a white solid of mp 126°C (lit. mp 128°C) (*25*); NMR ($CDCl_3$) δ 3.9 (*s*, 2H), 7.2-7.9 (*m*, 6H).

4,5-Phenanthrenedicarboxylic acid was prepared from the corresponding pyrenedione by a procedure similar to that reported for oxidation of fluoranthenequinone (*16*). 4,5-Pyrenedione (0.045 g, 0.195 mmole) was dissolved in 25 ml of tetrahydrofuran, and 10 ml of 30% H_2O_2 was added. After stirring overnight, the solution was acidified to pH 2 with hydrochloric acid and the product was extracted with methylene chloride, dried, and evaporated. Crystals (0.018, 35% yield) formed and were recrystallized from methanol: mp = 256°C (lit. mp = 258°C) (*22*). Mass spectrum of product after diazomethane treatment: *m/e* = 294(10), 235(100), 220(46).

Instruments and Apparatus

The gas chromatograph-mass spectrometer (GC-MS) was a Hewlett-Packard 5993B quadrupole, EI-70 eV equipped with an Avondale B capillary inlet and a 21 MX-E computer (ANSWER software). The GC/MS interface was modified to allow the entire effluent from a fused silica capillary columns to be drawn into the mass spectrometer. The column was either a 25 m (0.32 mm ID) SE-54 (siloxane, Hewlett-Packard) or a 15m (0.32 ID) polymethyl (5% phenyl) siloxane (J & W Scientific). Splitless injections were employed with 5-8 psi head pressure and 2 ml/min He carrier flow. A typical temperature program was 70 to 310°C at

10°C/min. The mass range scanned was 50 to 400 amu with a scan time of 1.6 sec.

The reversed-phase high performance liquid chromatography (HPLC) apparatus consisted of a Perkin-Elmer Series 3 microprocessor-controlled gradient system equipped with a Rheodyne 7105 injector. The analytical column was a Perkin-Elmer C-18 reversed-phase column, 0.26 × 25 cm (P.N. 089-0716). The column was surrounded by a glass jacket and the temperature was maintained at 27°C with a refrigerated/heated bath and circulator to insure reproducibility. A Waters Associates Model 440 fixed wavelength detector and a Perkin-Elmer LC-75 variable wavelength ultraviolet detector were connected in series. Data was acquired on a Waters Associates Data Module. In order to improve the useful sensitivity of this system in an in-line trap column was used. The trap column consisted of two 60 × 0.7 cm stainless steel columns packed with 37-75 μm C-18 Porasil B (Waters Assoc.) and was located between the water pump and the solvent-mixing coil. Acetonitrile was of HPLC grade (Fisher Scientific) and the water was obtained from a Millipore Corporation purification system (Milli-Q) fitted with an additional Continental Model 2021 canister.

Results and Discussion

Equilibria Considerations

The predominant chlorine-containing species in aqueous chlorine solutions are HOCl, OCl^-, Cl^-, Cl_2, and Cl_3^- (*26*). The relationships between the species are summarized by Eqs. (1), (2) and (3) (*27–29*). The OCl^- and HOCl concentrations are significant at pH greater than ~ 6 and the HOCl, Cl_2 and Cl_3^- concentrations are significant at pH less than ~ 6.

$$HOCl \leftrightharpoons H^+ = OCl^- \quad (1)$$

with

$$K_{HOCl} = 2.62 \times 10^{-8} \text{ at } 20°C$$

$$Cl_2 + H_2O \leftrightharpoons HOCl + H^+ + Cl^- \quad (2)$$

with

$$K_{Cl_2^-} = 3.38 \times 10^{-4} \text{ at } 20°C$$

$$Cl_2 + Cl^- \leftrightharpoons Cl_3^- \quad (3)$$

with

$$K_{Cl_3^-} = 0.19 \text{ at } 25°C$$

Table 1. Products of 1-methylnaphthalene reactions.

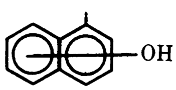
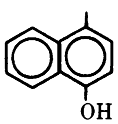
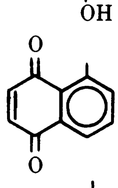
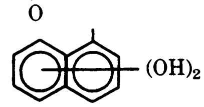
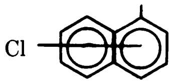
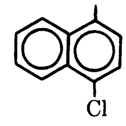
Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	Amt present pH 8[c]	*m/z* (relative abundance)
$C_9H_8O_2$	1.051	148	—	Minor	148 (6), 133 (15), 120 (4), 105 (100), 91 (18), 77 (89)
$C_9H_8O_2$	1.106	148	—	Trace	148 (7), 133 (71), 105 (100), 77 (55)
	1.458	158	Minor	—	158 (100), 143 (2), 141 (4), 130 (16), 129 (38), 128 (29), 127 (16), 115 (15), 103 (8), 102 (10)
	1.556	158	Minor	—	158 (100), 157 (70), 143 (1), 141 (3), 130 (13), 129 (30), 128 (39), 127 (18), 115 (15), 103 (6), 102 (5)
	1.355	172	Minor	—	172 (100), 157 (5), 144 (19), 127 (16), 117 (8), 116 (54), 115 (77), 90 (46), 89 (54), 63 (48)
	1.442	174	Minor	Trace	174 (10), 159 (100), 131 (39), 105 (12), 103 (28), 77 (33)
	1.358	176	Minor	—	176 (64), 178 (26), 141 (100), 138 (37), 115 (40)
	1.375[d]	176	Minor	Major	176 (65), 178 (24), 142 (12), 141 (100), 139 (36), 115 (34)

Table 1. *(continued)*

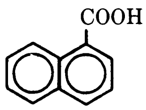
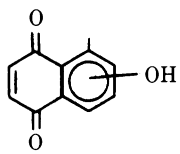
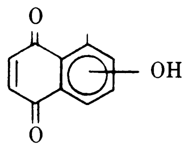
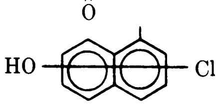
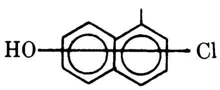
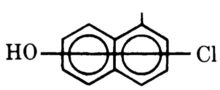
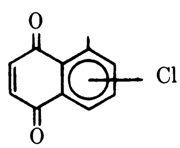
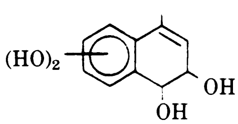
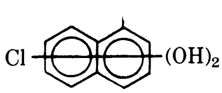
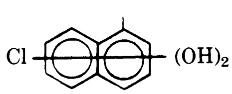
Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	pH 8[c]	*m/z* (relative abundance)
Unknown	1.587	?	—	Minor	181 (92), 183 (32), 147 (100), 91 (34), 90 (43), 89 (55), 70 (49)
	1.541[e]	186	—	Trace	186 (47), 155 (100), 127 (60)
	1.414	188	—	Minor	188 (72), 173 (100), 161 (28), 160 (87), 132 (19), 131 (43), 105 (34), 104 (21), 103 (31), 89 (79), 77 (51)
	1.511	188	—	Minor	188 (90), 160 (13), 132 (9), 131 (8), 119 (76), 104 (22), 103 (100), 91 (70), 90 (70), 89 (71), 77 (59)
	1.599	192	Minor	—	192 (100), 194 (37), 177 (1), 157 (85), 129 (38), 128 (75), 127 (61), 126 (21), 102 (24), 77 (36), 64 (50), 63 (54)
	1.880	192	Minor	—	192 (100), 194 (37), 177 (2), 163 (20), 157 (46), 139 (17), 129 (53), 128 (22), 127 (55), 126 (18), 102 (17), 101 (15), 77 (29), 76 (21), 75 (27), 74 (23), 63 (50)
	1.897	192	Minor	—	192 (100), 194 (37), 177 (2), 165 (9), 163 (22), 157 (42), 129 (38), 128 (55), 127 (45), 126 (15)
Unknown	1.582	?	—	Minor	195 (100), 197 (39), 180 (8), 178 (7), 160 (6), 143 (4), 131 (24), 115 (8), 103 (37), 89 (7), 77 (24)
	1.728	206	Minor	—	206 (71), 208 (25), 180 (8), 179 (8), 178 (17), 163 (8), 165 (2), 150 (20), 150 (17), 143 (22), 126 (8), 124 (23), 115 (100), 114 (18), 89 (49), 87 (22), 86 (22), 75 (17), 74 (18), 73 (14), 63 (52)
	1.496	208	—	Minor	208 (5), 190 (9), 175 (26), 167 (34), 165 (100), 147 (15), 145 (12), 129 (12), 115 (18)
	1.481	208	Major	—	208 (10), 210 (4), 182 (16), 180 (40), 167 (16), 165 (41), 145 (100), 144 (23), 116 (17), 115 (40), 102 (41), 101 (43), 77 (25), 75 (50)
	1.772	208	Minor	—	208 (8), 210 (4), 195 (30), 193 (76), 173 (100), 167 (8), 165 (19), 157 (24), 155 (11), 129 (15), 128 (10), 127 (17), 115 (15), 105 (50), 102 (35), 101 (36)

Table 1. *(continued)*

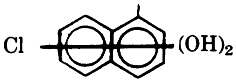
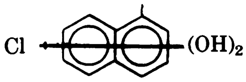
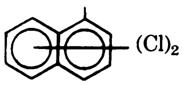
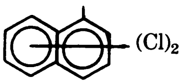
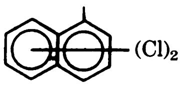
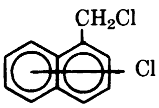
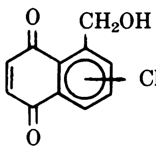
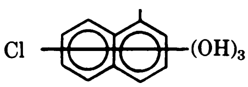
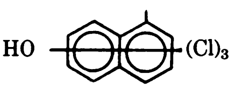
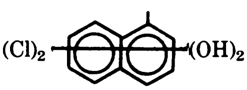
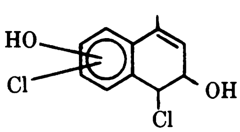
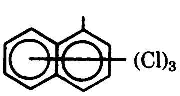
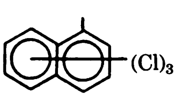
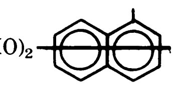
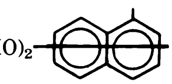
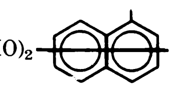
Proposed structure	Relative retention time (GC)[a]	Molecular ion, m/z	Amt present		m/z (relative abundance)
			pH 3[b]	pH 8[c]	
	1.784	208	Minor	Minor	208 (11), 210 (4), 195 (29), 193 (80), 173 (100), 167 (8), 165 (22), 157 (24), 155 (11), 129 (15), 128 (12), 127 (18), 115 (20), 105 (44), 102 (32), 101 (29)
	1.797	208	Minor	—	208 (72), 210 (20), 182 (6), 180 (14), 167 (19), 165 (25), 155 (17), 154 (27), 153 (36), 152 (88), 145 (34), 124 (71), 117 (44), 115 (11), 103 (18), 89 (87) 62 (100)
	1.674	210	Major	Trace	210 (57), 212 (34), 177 (35), 175 (100), 149 (14), 139 (70), 113 (8)
	1.686	210	Major	Trace	210 (60), 212 (35), 177 (33), 175 (100), 151 (4), 149 (14), 139 (56), 113 (6)
	1.712	210	Minor	Trace	210 (43), 212 (24), 177 (33), 175 (100), 139 (38)
	1.804	210	Minor	—	210 (60), 212 (33), 177 (37), 175 (100), 149 (16), 139 (52)
	1.812	222	—	Trace	222 (63), 224 (23), 223 (16), 221 (28), 207 (8), 205 (10), 187 (23)
	1.694	224	—	Major	224 (3.8), 226 (1.4), 209 (9), 189 (18), 183 (5), 181 (16), 173 (13), 171 (23), 161 (100), 149 (11), 147 (24), 143 (35), 91 (39), 89 (52), 77 (74)
	1.916	226	Minor	—	216 (100), 228 (56), 211 (4), 209 (5), 193 (29), 192 (34), 191 (72), 173 (11), 165 (17), 164 (25), 163 (45), 162 (52), 137 (4), 128 (51), 127 (85), 126 (58), 113 (8)
	1.855	242	—	Minor	242 (15), 244 (8), 209 (4), 207 (16), 181 (36), 179 (92), 171 (37), 143 (18), 116 (38), 115 (100), 89 (38)
	1.820	244	Minor	—	244 (4), 246 (3), 211 (22), 210 (14), 209 (54), 208 (16), 193 (25), 192 (17), 191 (30), 180 (15), 179 (23), 173 (100), 165 (30), 163 (39), 162 (23), 157 (13), 145 (22), 142 (42), 129 (20), 128 (44), 127 (42), 126 (18), 117 (17), 116 (18), 115 (62)
	1.945	244	Minor	—	244 (50), 246 (49), 211 (68), 210 (20), 209 (100), 185 (9), 183 (13), 175 (29), 173 (67), 137 (22)
	1.961	244	Minor	—	244 (55), 246 (56), 211 (70), 209 (100), 185 (11), 183 (18), 175 (28), 173 (69), 137 (25)

Table 1. *(continued)*

Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	Amt present pH 8[c]	*m/z* (relative abundance)
$C_{13}H_{15}O_3Cl$[e] or $C_{12}H_{11}O_4Cl$[e]	2.294	254	Minor	—	254 (26), 256 (10), 241 (34), 239 (100), 218 (10), 211 (9), 209 (19), 208 (17), 207 (65), 206 (32), 203 (7), 195 (13), 193 (11), 175 (15), 171 (26), 163 (16), 159 (37), 147 (65), 143 (21), 135 (15), 115 (42), 105 (46)
$C_{11}H_{13}O_5Cl$[c]	2.370	260	Minor	—	260 (100), 262 (36), 261 (55), 259 (81), 246 (0.4), 244 (3), 233 (4), 231 (10)
$C_{11}H_{13}O_5Cl$[e]	2.441	260	Minor	—	260 (100), 262 (36), 261 (49), 259 (86), 233 (6), 231 (10)
$(HO)_2$  $(Cl)_3$	1.968	276	—	Trace	276 (48), 278 (53), 243 (4), 241 (10), 226 (3), 215 (51), 214 (20), 213 (100), 212 (20), 207 (9), 205 (52), 187 (19), 185 (24), 179 (30), 177 (96), 152 (10), 151 (10), 150 (30), 149 (27), 115 (28)
$(HO)_2$  $(Cl)_3$	2.081	276	—	Trace	276 (39), 278 (43), 243 (4), 241 (13), 215 (57), 214 (15), 213 (100), 205 (42), 197 (13), 187 (2), 185 (16), 150 (22), 149 (43), 148 (13), 115 (62)
$(HO)_2$  $(Cl)_3$	2.160	276	—	Trace	276 (39), 278 (39), 243 (13), 241 (20), 226 (5), 215 (56), 214 (11), 213 (100), 205 (51), 187 (16), 185 (17), 178 (34), 177 (50), 150 (24), 149 (62), 115 (70), 114 (35)

[a]Reference = 1-methylnaphthalene.
[b]pH = 3.0, [1-methylnaphthalene] = 2×10^{-5} [total chlorine] = 1×10^{-3}, 96 hr required for 3 half-lives.
[c]pH = 8.0, [1-methylnaphthalene] = 2×10^{-5} [total chlorine] = 1×10^{-3}, 1 hr required for 2 half-lives.
[d]Relative retention time (GC) and mass spectrum identical to those of an authentic standard.
[e]Derivatized with diazomethane prior to GC/MS analysis.

An anticipated difference in reaction kinetics and reaction mechanisms between low and high pH chlorination reactions of PAH has already been noted (*30*). In the present study, therefore, the product distributions for each compound were determined at both pH 3 and pH 8 in order to insure the maximum probability for observing products formed by all reactive chlorine species.

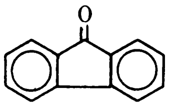
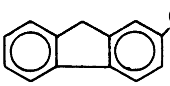
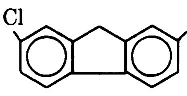
Products

The products observed are listed in Tables 1–8 along with their mass spectral data. In most cases the product distributions were determined after the PAH ($\sim 10^{-5}$ *M*) was allowed to react with $\sim 10^{-3}$ *M* chlorine for five to seven half lives (specific conditions are included in the tables). A small amount of acetonitrile (1 to 8%) was used in many reactions to provide sufficient quantities of PAH products for analysis and to minimize the formation of PAH crystals during a reaction. The use of such small amounts of this organic solvent did not appear to alter the product distribution based on chromatographic comparison with reactions in the absence of acetonitrile. In contrast, reaction solutions containing crystalline PAH material tended to result in the formation of only chloro products rather than both the chloro and oxygenated products observed in homogeneous solutions.

Reactions at high pH tended to produce oxygenated products while those at low pH tended to give both oxygenated and chlorinated products. The predominant product types included mono- and dichlorosubstituted compounds, quinones, phenols, carboxylic acids, and an epoxide. Minor compound types included chlorohydrins and dihydrodiols. A detailed mechanistic investigation of phenanthrene suggested the formation of an arene oxide as the key intermediate in interpreting the product distribution.

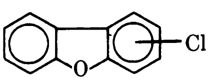
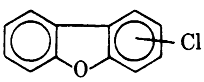
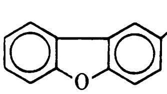
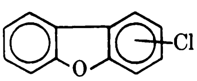
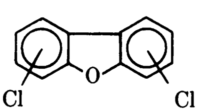
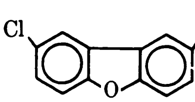
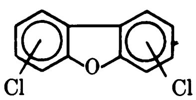
Free-radical substitution on the methyl groups of 1-methylphenanthrene and 1-methylnaphthalene and the benzylic carbon of fluorene was not extensive. This type of reaction which results in the formation of benzyl halides and alcohols has previously been reported for some chlorination reactions (*31*). Benzyl alcohols can be distinguished from ring-substituted

Table 2. Products of fluorene reactions.

Proposed structure	Relative retention time (HPLC)[a]	Molecular ion, m/z	Amt present		m/z (relative abundance)
			pH 3[b]	pH 8[c]	
 [d]	0.903	180	—	~ 2%[e]	—
 [d,f]	1.097	200	44%[e]	—	200 (44), 202 (14), 166 (29), 165 (100), 164 (43), 163 (58)
 [d,f]	1.184	234	10%[e]	—	234 (20), 236 (18), 201 (50), 199 (100), 165 (20), 164 (24), 163 (54)

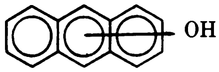
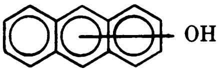
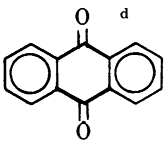
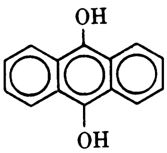
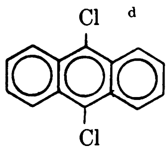
[a]Reference = fluorene.
[b]pH = 3.05, [fluorene] = 1.38×10^{-6}, [total chlorine] = 4.21×10^{-4}, 360 min required for 4.5 half-lives.
[c]pH = 7.70, [fluorene] = 1.38×10^{-6}, [total chlorine] = 4.01×10^{-4}, 7 days required for 2 half-lives.
[d]HPLC retention time and $^{a}254/^{a}280$ identical to those of an authentic standard.
[e]The percent yields were determined by HPLC utilizing authentic compounds as standards.
[f]Relative retention time and mass spectrum identical to those of an authentic standard.

Table 3. Products of dibenzofuran reactions.

Proposed structure	Relative retention time (HPLC)[a]	Molecular ion, m/z	Amt present		m/z (relative abundance)
			pH 3[b]	pH 8[c]	
	1.168	202	Trace	—	202 (100), 204 (50), 175 (6), 173 (10), 167 (7), 139 (61)
	1.190	202	Minor	—	202 (100), 204 (45), 175 (3), 173 (8), 167 (4), 139 (62)
 [d]	1.212	202	Major	Major	202 (100), 204 (40), 175 (3), 173 (5), 167 (3), 139 (45)
	1.225	202	Minor	—	202 (100), 204 (45), 175 (3), 176 (3), 167 (2), 139 (43)
	1.389	236	Minor	—	236 (100), 238 (53), 203 (4), 201 (6), 175 (33), 173 (81, 147 (11), 138 (37), 137 (46)
 [d]	1.405	236	Major	—	236 (100), 238 (53), 203 (2), 201 (5), 175 (23), 173 (55), 147 (5), 138 (22), 137 (27)
	1.414	236	Minor	—	236 (100), 238 (54), 203 (4), 201 (7), 175 (37), 173 (93), 147 (10), 138 (38), 137 (44)

[a]Reference = dibenzofuran.
[b]pH = 3.04, [dibenzofuran] = 2×10^{-5}, [total chlorine] = 1×10^{-3}, 4 hr required for 4 half-lives.
[c]pH = 8.0, [dibenzofuran] = 2×10^{-5}, [total chlorine] = 1×10^{-3}, less than 50% of starting material reacted in one week.
[d]Relative retention time and mass spectrum are identical to those of an authentic standard.

Table 4. Products of anthracene reactions.

Proposed structure	Relative retention time (GC)[a]	Molecular ion, m/z	Amt present pH 3[b]	Amt present pH 8[c]	m/z (relative abundance)
	1.094	194	—	Trace	194 (73), 165 (100), 163 (25), 83 (31), 62 (34)
	1.123	194	—	Trace	194 (100), 165 (71)
 [d]	1.182	208	Major	Major	208 (48), 207 (16), 180 (72), 153 (10), 152 (74), 151 (40), 150 (23), 126 (12), 76 (100), 74 (56)
	1.263	210	Major	Minor	210 (75), 209 (22), 208 (15), 193 (8), 181 (100), 165 (33), 163 (20), 153 (22), 152 (8), 151 (24), 150 (11), 105 (33), 104 (19), 77 (83), 76 (89), 63 (35)
 [d]	1.317	246	Minor	—	246 (52), 248 (28), 213 (24), 212 (5), 211 (6), 210 (10), 176 (100), 174 (45), 150 (17), 149 (10), 124 (10), 123 (25), 122 (18)

[a]Reference = anthracene.
[b]pH = 3.0, [anthracene] = 1.99×10^{-6}, [total chlorine] = 1.0×10^{-3}, 30 min were required for 7 half-lives, 4% acetonitrile.
[c]pH = 8.0, [anthracene] = 1.99×10^{-6}, [total chlorine] = 1.0×10^{-3}, 30 min were required for 7 half-lives, 4% acetonitrile.
[d]Relative retention time and mass spectrum are identical to those of an authentic standard.

Table 5. Products of phenanthrene reactions.

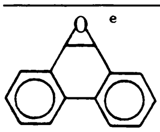
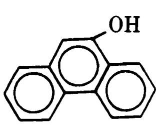
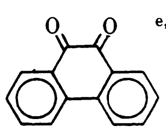
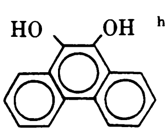
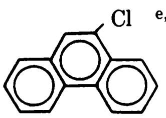
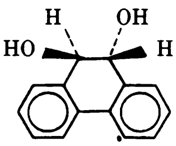
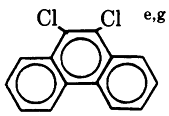
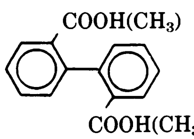
Structure	Relative retention time (HPLC)[a]	Relative retention time (GC)[a]	Molecular ion, m/z	Amt present pH 3[b,c]	Amt present pH 8[c,d]	m/z (relative abundance)
 [e]	0.816	—	194	—	88%[f]	————
 [e]	0.816	—	194	19%	~ 2%[f]	————
 [e,g]	0.726	1.291	208	32%	2%	208 (14), 180 (100), 152 (57), 151 (29), 150 (20)
 [h]	—	1.080	210	—	Minor	210 (2), 181 (100), 153 (15), 152 (39)

Table 5. *(continued)*

Structure	Relative retention time (HPLC)[a]	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b,c]	Amt present pH 8[c,d]	*m/z* (relative abundance)
 [e,g]	1.128	—	212	34%	—	212 (93), 214 (33), 177 (36), 176 (62), 174 (15), 88 (100), 75 (60)
 [e,g]	0.614	1.235	212	—	3%	212 (20), 194 (22), 181 (62), 166 (66), 165 (100), 163 (11), 152 (25)
 [e,g]	1.251	—	246	7%	—	246 (100), 248 (72), 212 (7), 211 (12), 210 (16), 177 (15), 176 (92), 175 (40), 174 (34)
 [g,i]	—	1.200	270	—	Minor	270 (4), 239 (4), 211 (100), 180 (8)

[a]Reference = phenanthrene.
[b]pH = 3.03, [phenanthrene] = 8.25×10^{-7}, [total chlorine] = 4.46×10^{-4}, 20 min required for 6 half-lives.
[c]The per cent yields were determined by HPLC utilizing authentic compounds as standards.
[d]pH = 7.70, [phenanthrene] = 6.60×10^{-7}, [total chlorine] = 7.73×10^{-4}, 90 min required for 8 half-lives.
[e]HPLC retention time and A_{254}/A_{280} identical to those of an authentic standard.
[f]Calculated from absorbance data at 254 and 280 nm.
[g]Relative retention time and mass spectrum are identical to those of an authentic standard.
[h]Proposed structure.
[i]Derivatized with diazomethane prior to GC/MS analysis.

Table 6. Products of 1-methylphenanthrene reactions.

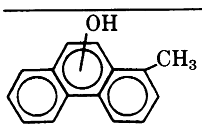
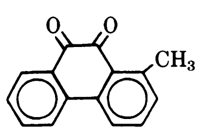
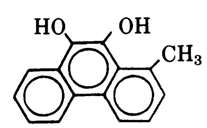
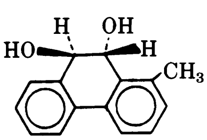
Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	Amt present pH 8[c]	*m/z* (relative abundance)
	1.188	208	Minor	Major	208 (100), 207 (22), 180 (19), 179 (39), 178 (44), 165 (68)
	1.197	222	Major	Major	222 (62), 194 (76), 165 (100), 163 (18)
	1.108	224	—	Trace	224 (27), 209 (49), 181 (9), 83 (100)
	1.117	226	—	Major	226 (34), 208 (37), 195 (74), 180 (34), 179 (51), 178 (40), 176 (13), 165 (100), 152 (23)

Table 6. *(continued)*

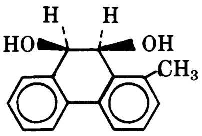
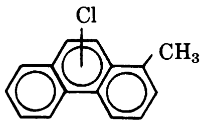
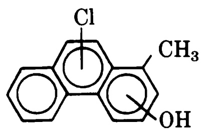
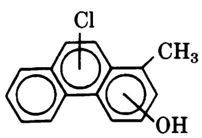
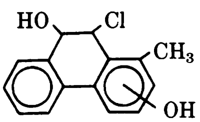
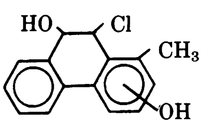
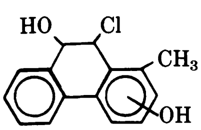
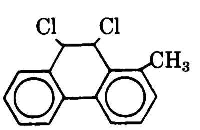
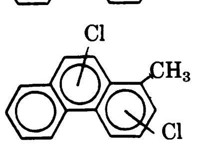
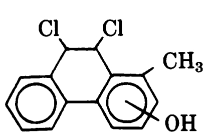
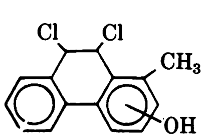
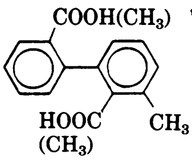
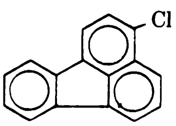
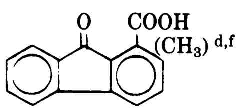
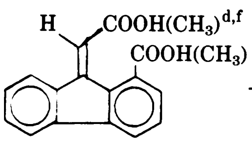
Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present: pH 3[b]	Amt present: pH 8[c]	*m/z* (relative abundance)
	1.125	226	—	Minor	226 (50), 209 (20), 208 (63), 207 (14), 195 (83), 181 (27), 180 (35), 179 (52), 178 (41), 176 (11), 165 (100), 152 (23)
	1.115	226	Minor	—	226 (87), 228 (22), 191 (100), 189 (78), 187 (19), 165 (16), 164 (12), 163 (17)
	1.293	242	Minor	—	242 (92), 244 (26), 207 (33), 179 (100), 178 (70), 176 (28)
	1.305	242	Trace	—	242 (100), 244 (27), 207 (52), 179 (77), 178 (64), 176 (30)
	1.217	260	Minor	—	260 (43), 262 (15), 244 (9), 242 (32), 231 (10), 229 (30), 226 (16), 225 (79), 215 (9), 213 (26), 207 (36), 195 (18), 194 (25), 179 (100), 178 (61), 176 (17), 165 (77), 163 (19), 152 (23)
	1.238	260	Trace	—	260 (60), 262 (22), 244 (14), 242 (47), 231 (21), 229 (68), 225 (5), 215 (9), 213 (21), 207 (55), 195 (15), 194 (27), 179 (100), 178 (67), 176 (21), 165 (81), 163 (25), 152 (22)
	1.246	260	Trace	—	260 (34), 262 (12), 244 (12), 242 (43), 231 (12), 229 (40), 225 (3), 215 (8), 213 (17), 207 (45), 195 (11), 194 (15), 179 (100), 178 (68), 176 (22), 165 (59), 163 (18), 152 (25)
	1.221	260	Major	—	260 (82), 262 (57), 227 (16), 225 (51), 190 (61), 189 (100), 187 (34)
	1.230	260	Minor	—	260 (100), 262 (68), 227 (24), 225 (70), 190 (32), 189 (64), 187 (21)
	1.174	278	Minor	—	278 (27), 280 (19), 244 (7), 243 (12), 242 (18), 229 (13), 227.(13), 226 (15), 225 (33), 208 (31), 207 (15), 191 (18), 190 (19), 189 (28), 179 (100), 178 (71), 176 (24), 165 (35), 163 (16), 152 (13)
	1.179	278	Trace	—	278 (43), 280 (31), 245 (35), 244 (26), 242 (36), 226 (16), 191 (19), 190 (18), 189 (27), 179 (34)

Table 6. *(continued)*

Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	Amt present pH 8[c]	*m/z* (relative abundance)
 [d]	1.006	284	Trace	Major	284 (4), 252 (18), 226 (12), 225 (68), 210 (19), 209 (12), 194 (31), 193 (44), 181 (30), 179 (19), 165 (100)

[a]Reference = 1-methylphenanthrene.
[b]pH = 3.0, [1-methylphenanthrene] = 1.39×10^{-5}, [total chlorine] = 1.0×10^{-3}, 1 hr required for 7 half-lives.
[c]pH = 8.0, [1-methylphenanthrene] = 1.39×10^{-5}, [total chlorine] = 1.0×10^{-3}, 23 hr required for 7 half-live
[d]Treated with diazomethane prior to analysis by GC/MS.

Table 7. Products of fluoranthene reactions.

Proposed structure	Relative retention time (HPLC)[a]	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	Amt present pH 8[c]	*m/z* (relative abundance)
 [d]	1.140	—	236	72%[e]	—	236 (100), 238 (29), 201 (32), 200 (50), 199 (13), 198 (15), 100 (18)
 [d,f]	—	1.064	238	—	Major	238 (29), 208 (18), 207 (75), 180 (69), 179 (48), 152 (28), 151 (72), 150 (56), 75 (100)
 [d,f]	—	1.247	294	—	Minor	294 (19), 236 (20), 235 (100), 220 (40)

[a]Reference = fluoranthene.
[b]pH = 2.99, [fluoranthene] = 3.32×10^{-7}, [total chlorine] = 3.03×10^{-4}, 242 min required for 4 half-lives.
[c]pH = 8.00, [fluoranthene] = 1.29×10^{-6}, [total chlorine] = 1.82×10^{-3}, 19 hr required for 4 half-lives.
[d]Relative retention time and mass spectrum are identical to those of an authentic standard.
[e]Determined by HPLC utilizing an authentic compound as a standard. 7% unreacted fluoranthene.
[f]Derivatized with diazomethane prior to GC/MS analysis.

Table 8. Products of pyrene reactions.

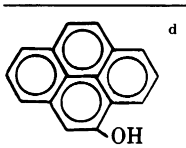
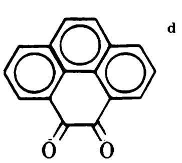
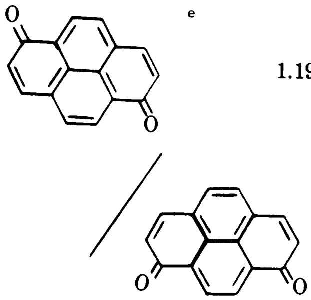
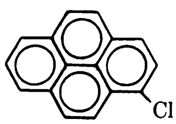
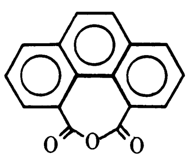
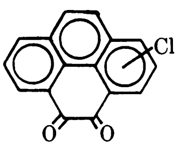
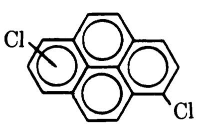
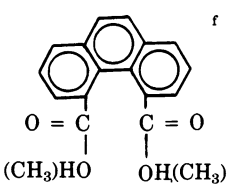
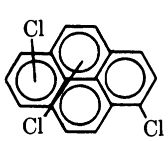
Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	Amt present pH 8[c]	*m/z* (relative abundance)
 [d]	1.178	218	—	Minor	218 (46), 189 (64), 187 (20), 95 (100)
 [d]	1.190	232	Major	Minor	232 (40), 204 (100), 176 (55), 175 (31), 174 (21), 150 (22), 111 (5), 99 (9), 88 (57)

Table 8. *(continued)*

Proposed structure	Relative retention time (GC)[a]	Molecular ion, *m/z*	Amt present pH 3[b]	Amt present pH 8[c]	*m/z* (relative abundance)
 [e]	1.196/1.20	232	—	Trace	232 (100), 204 (29), 176 (75), 174 (18), 150 (15), 88 (30) 232 (100), 204 (25), 176 (70), 174 (17), 150 (13), 88 (27)
 [d]	1.109	236	Major	Major	236 (14), 238 (12), 201 (59), 200 (77), 100 (100)
 [d]	1.200	248	—	Trace	248 (13), 204 (77), 176 (62), 175 (56), 174 (22), 150 (16), 88 (100)
	1.250	266	Minor	—	266 (6), 268 (3), 240 (8), 238 (23), 212 (4), 210 (15), 176 (40), 175 (69), 174 (70), 99 (41), 98 (46), 87 (100)
	1.172	270	Major	Trace	270 (16), 272 (11), 237 (1), 235 (4), 200 (47), 198 (25), 100 (100)
 [f]	1.217	294	—	Major	294 (1), 235 (41), 176 (29), 163 (52)
	1.234	304	Trace	—	304 (12), 306 (16), 307 (12), 200 (32), 199 (48), 74 (10)

[a]Reference = pyrene.
[b]pH = 3.0, [pyrene] = 7.1×10^{-6}, [total chlorine] = 1.20×10^{-3}, 30 min required for 7 half-lives, 8% acetonitrile.
[c]pH = 8.00, [pyrene] = 6.60×10^{-6}, [total chlorine] = 1.10×10^{-3}, 90 min required for ~ 4 half-lives, 8% acetonitrile.
[d]Relative retention time and mass spectrum are identical to those of an authentic standard.
[e]Mass spectra and relative retention times were identical to data obtained for an authentic mixture of 1,6-and 1,8- pyrenediones.
[f]Treated with diazomethane prior to GC/MS analysis.

isomers on the basis of prominent M-OH, M-1, M-2 and M-3 peaks in their mass spectra (*32*). In contrast, 1-chloromethylnaphthalene exhibits a mass spectrum which is nearly identical to that of its ring substituted isomer, 1-chloro-4-methylnaphthalene. Fortunately, a difference in relative gas chromatograph (GC) retention time (1.45 versus 1.38, respectively) allowed the conclusion that the former methyl-substituted halide was not produced in either 1-methylnaphthalene experiment. However, it is not possible to ascertain from the present data whether any of the other chloromethyl derivatives of naphthalene or phenanthrene were formed. A hydroxymethyl group is probably present in only one trace product of methylnaphthalene (Table 1, $M^{+\cdot} = 222$).

Biological Implications

An assessment of the biological implications of release of these chlorination products into the environment and into drinking water must, at present, depend upon scattered literature reports of various screening tests on individual compounds. These reports indicate that nearly all of the compound types produced in the chlorination reactions of PAH have the potential for causing adverse biological response. However, it is not possible to accurately predict activity of untested products because the nature of the various substituents and their locations on the aromatic ring may drastically affect the biological activity (*33*).

All of the nonchlorine-containing products of phenanthrene (except diphenic acid) shown in Table 5 have been tested for mutagenic activity by the reversion of histidine-dependent *Salmonella typhimurium* and the rec assay with *Bacillus subtilis* (*34*, *35*). The strongest mutagenic activity was observed with phenanthrene-9,10-oxide and 9-phenanthrenol, but this activity was much less than that of the control, benzo[a]pyrene-4,5-oxide. Lack of significant mutagenicity and tumorigenicity of the epoxide and *trans*-dihydrodiol of phenanthrene was reported by other laboratories (*36*).

The 1,6- and 1,8-pyrenediones have been reported to be mutagens and enhancing agents to other mutagens (*37*). Anthraquinone shows little or no activity (*38*), but certain derivatives (e.g., phenols) are quite mutagenic (*39*). Quinones of benzo(a)pyrene are mutagenic and the Ames assay without microsomal activation (*40*).

Phenols may be carcinogenic, mutagenic and toxic (*18*) and may bind to DNA, RNA and proteins (*41*). Chlorophenols may also exhibit similar activity (*42*). 2-Naphthol is known to affect the function of renal tubules (*43*), and 1-naphthol is a reported mutagen (*38*).

Chlorinated PAH s (e.g., chlorinated dibenzofurans) may be extremely toxic (*44*, *45*). Chloromethyl-(*46*) and hydroxymethyl-substituted PAHs (*47*) may also have mutagenic and carcinogenic activity.

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